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TITLE: RESONANCES IN ELECTRON-MOLECULE SCATTERING AND PHOTOIONIZATION

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RESONANCES IN ELECTRON-MOLECULE SCATTERING AND PHOTOIONIZATION

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The development of reliable theoretical models for calculating the decay of quasi-stationary states of molecular systems has become an important endeavor for theoretical chemists. The understanding and analysis of a wide variety of physical and chemical phenomena depend on a knowledge of the behavior of these states in both collisional and photoionization problems. In this article we describe the theory and calculation of these cross sections using our Linear Algebraic/Optical Potential method. The theory makes optimal use of the numerical methods developed to solve large sets of coupled integral equations and the bound state techniques used by quantum chemists. Calculations are presented for a representative class of diatomic and triatomic molecules at varying levels of sophistication and for collisional and photoionization cross sections.

Introduction

The formation and subsequent decay of highly excited neutral molecules and molecular negative ions plays an important role in many physical and chemical problems (1,2,3). These metastable states are formed when electrons collide with or are ejected from molecular systems. Consequently they are seen in photoionization cross sections (4,5) as well as collisional excitation problems involving electronic, (6) vibrational, (7) and dissociative channels (8). The quasi-stationary nature of these temporary states has interested theoretical chemists for many years. In fact a large number of the early predictions and calculations of the energies of these states were based on variants of bound state techniques used widely in quantum chemistry. These methods exploited the localized nature of the resonant scattering wavefunction. Later methods such as the Stieltjes imaging (5,6) and complex co-ordinate techniques (9,10) went further and calculated the lifetime (width) of these metastable states. However it should be recognized that these resonant states are a subset of those treated by more standard collisional techniques. Methods such as the close coupling (11)

Kohn-variational (12), Schwinger-variational, (13) R-Matrix (14), and linear algebraic techniques (15,16) have been quite successful in calculating collisional and photoionization cross sections in both resonant and nonresonant processes. These approaches have the advantage of generality at the cost of an explicit treatment of the continuous spectrum of the Hamiltonian and the requisite boundary conditions. In the early molecular applications of these scattering methods, a rather direct approach based on the atomic collision problem was utilized which lacked in efficiency. However in recent years important conceptual and numerical advances in the solution of the molecular continuum equations have been discovered which have made these approaches far more powerful than those of a decade ago (13,15,16). These new methods make extensive use of the ideas of bound state quantum chemistry to treat electron exchange, polarization and correlation (17,18). On the other hand they treat the molecular scattering function either numerically or in a basis set of numerical continuum functions (19). This has the advantage of providing an accurate representation of the molecular continuum function without causing undue strain on the numerical representation. In the next section we develop one of these approaches, the linear algebraic/optical potential method (LAMOPT) (15), in some detail. The last section is devoted to discussing the numerous applications to photoionization and electron scattering which have been made with the method as well as some earlier work on $e+N_2$ vibrational excitation (7) using the R-matrix technique.

Theoretical Methods

One of the more important features underlying all of the theoretical approaches used in the molecular continuum problem is the division of space into a strongly and weakly intereacting part. This division may be performed in function space as in the early "stabilization" method (3) or in co-ordinate space as in the R-matrix method (14). In the strongly interacting subspace, it is necessary to deal with all the complications of the full many-body problem. However, the strength of the interaction in this region is such that the difference between bound and continuum states is not substantial. These facts are what led to the early successes of the stabilization, Stieltjes and complex co-ordinate methods in treating resonances. The difficulties of applying these approaches to the entire molecular continuum led to the development of more powerful techniques. The R-matrix method, which had some spectacular successes for atomic collisions (20), seemed an excellent choice to fill the void. One of the most attractive features of the method is its use of a discrete basis set to expand the continuum orbital in the inner R-matrix region. The application of the standard Gaussian and Slater basis sets in the R-matrix formalism was made practical by the use of the Bloch -operator formalism (2 ,22). This was successful in a number of cases (23,24,25) most notably $e-N_2$ scattering. However certain difficulties arose which pointed to the need of more general and flexible basis sets for rapid (practical) convergence. In spite of these difficulties the physical division of space into an internal and external region remains viable. The R-matrix formalism allows the division

exploiting the different physics of the two regions optimally and adapting the mathematics to accomplish the purpose in the most efficient manner. We proceed by defining

$$(\mathscr{H} + \mathscr{L}_b - E)|\psi) = \mathscr{L}_b|\Psi) \tag{1a}$$

in the internal region, where

$$\mathscr{H} = \mathscr{H}_T + T_e + V_{eT} + T_R \tag{1b}$$

$$\mathscr{H}_T = \text{Target electronic Hamiltonian} \tag{1c}$$

$$T_e = \text{Kinetic energy of the scattering electron} \tag{1d}$$

$$V_{eT} = \text{Electronic potential} = -\sum_q^{n_q} \frac{Z_q}{|\vec{R}_q - \vec{r}_e|} + \sum_{i=1}^{n} \frac{1}{|\vec{r}_e - \vec{r}_i|} \tag{1e}$$

$$T_R = \text{Nuclear kinetic Energy} = -\frac{1}{2} \sum_q \nabla^2_{R_q} \tag{1f}$$

$$\mathscr{L}_b = \frac{1}{2} \sum_c |c)\, \delta(r_e - a)\, \left(\frac{\partial}{\partial r_e} - b\right)(c| \tag{1g}$$

$$a = \text{R-matrix radius} \tag{1h}$$

$$b = \text{Surface log derivative} \tag{1i}$$

and $|c)$ is a target eigenfunction of $\mathscr{H}_T$.

Aside from the Bloch $\mathscr{L}$-operator, $\mathscr{L}_b$, which is added and subtracted to the Hamiltonian to ensure Hermicity, the division into target and incident particle Hamiltonian is standard. In equation (1g) we have only allowed for open electronic channels. A Bloch operator for the nuclear coordinate would need to be added if dissociation were included. A formal solution to the problem may be written as

$$|\Psi) = g\, \mathscr{L}_b|\psi) \tag{2a}$$

where

$$g = (\mathscr{H} + \mathscr{L}_b - E)^{-1} \tag{2b}$$

By projecting equation (2a) onto the channels, $|c)$, we obtain

$$F_c(r) = \sum_{c'} g_{cc'}(r|a)\, \left(\frac{\partial F_{c'}}{\partial r} - bF_{c'}\right)_a \,, \tag{3}$$

and setting r=a, we get

$$F_c(a) = \sum_{c'} \mathscr{R}_{cc'}\left(\frac{\partial F_{c'}}{\partial r} - bF_{c'}\right)_a \tag{4a}$$

$$\mathscr{R}_{cc'} = g_{cc'}(a|a) = \text{R-matrix} \tag{4b}$$

If one knows the functional form of F_c at r=a it is possible by a simple matching procedure to extract the scattering information. Alternatively, it is possible to devise numerical procedures to propagate the R-matrix from r=a to very large values of the radial coordinate. At these values of r, a matching to free waves is possible. In order to do this it is necessary that the coupling potential be local beyond r=a. In addition, if it is weak and multipolar in form, the R-matrix propagation method (26,27) can be made very efficient. In essense then the difficult part of the calculation is the construction of the Green's function inside the spherical surface r<a. As is true of all boundary value problems there are essentially two methods for the construction of the Green's function. The first and perhaps most sraightforward is to construct solutions of the problem.

$$(\mathscr{H} + \mathscr{L}_b - E_i)|\Psi_i) = 0 \tag{5}$$

which enables us to write

$$g_{cc'}(r|r') = \sum_i \frac{\gamma_{ci}(r)\gamma_{c'i}(r')}{E_i - E} \tag{6}$$

This spectral form has the advantage that a single diagonalization of the Hamiltonian allows one to construct easily the R-matrix at all energies. In order to accomplish this it is necessary to introduce a basis set of many-electron functions and solve equation (5) variationally (23,24,25). The many-electron functions themselves are constructed as products of one-electron orbitals, expanded in some primitive basis set. For molecular systems with more than one nuclear center the use of multicenter Gaussian or Slater functions does much in representing the continuum function near the nuclei. However these functions are not particularly good at representing the scattering function away from the nuclei where they oscillate rather than decay as true bound states. Thus one is faced with the following dilemma: use large traditional basis sets of Slater and/or Gaussian functions for which it is possible to do the one and two electron integrals efficiently or look for a better representation. By a better representation we mean either a more efficient one-electron basis to expand the molecular continuum function or an alternative procedure for the solution of the equation for the Green's function. In searching for a better representation it should be realized that some of the numerical procedures might have to be replaced by others which are not quite

so "simple" or efficient. Thus, for example, the use of numerical continuum orbitals within the R-matrix formalism requires the use of single-center expansion techniques and numerical quadratures for certain classes of one and two-electron matrix elements. For diatomics the procedure can be made reasonably efficient but for polyatomics the jury is still out. The approach we have pursued is rooted in the second method for the construction of the Green's function. If we return to the integral equation (2) and divide the Hamiltonian into an unperturbed ($\mathscr{H}_0$) and perturbed (V) part, we may write

$$|\Psi) = (G_0 + G_0 Vg)\mathscr{L}_b|\Psi) \tag{7a}$$

$$= G_0\mathscr{L}_b|\Psi) + G_0 V|\Psi)$$

where

$$G_0 = (\mathscr{H}_0 + \mathscr{L}_b - E)^{-1} \tag{7b}$$

The division of the Hamiltonian into an unperturbed and perturbed part is of course arbitrary. However in most cases $_0$ is chosen to make the scattering particle Green's function simple to calculate. Typical choices would be the target plus a free particle or in the case of positive ions, target plus Coulomb wave. Equation (7) has a particularly simple structure for the scattering of an electron from a static potential. The basic starting point is the expansion of the wavefunction, Green's function and potential in spherical harmonics. In contrast to atomic scattering problems, the potential is not diagonal in the angular momentum quantum number of the scattered electron ℓ. This leads to the following set of coupled integral equations,

$$\Psi_\ell(r) = G_\ell(r|a)\left(\frac{\partial\Psi_\ell}{\partial r} - b\Psi_\ell\right)_{r=a} + \sum_{\ell'} \int G_\ell(r|r')V_{\ell\ell'}(r')\Psi_{\ell'}(r')dr' \tag{8a}$$

where

$$G_\ell(r|r') = R_\ell(r_<)I_\ell(r_>) \tag{8b}$$

The Green's function is chosen to satisfy the boundary condition demanded by the R-matrix method. This is easily accomplished by choosing $R_\ell(r)$ to be regular at the origin and requiring

$$\frac{dI_\ell}{dr} = bI_\ell \tag{8c}$$

at r=a. The linear algebraic method proceeds by introducing a quadrature scheme into the set of equations (8a) to get

$$\Psi_\ell(r_i) = G_\ell(r_i|a)\left(\frac{\partial\Psi_\ell}{\partial r} - b\Psi_\ell\right)_a + \sum_{\ell' j} G_\ell(r_i|r_j)W_j V_{\ell\ell'}(r_j)\Psi_{\ell'}(r_j) \tag{9}$$

By defining

$$\mathcal{M}_{\ell i,\ell' j} = \delta_{\ell\ell'}\delta_{ij} - G_\ell(r_i|r_j)W_j V_{\ell\ell'}(r_j) \quad , \tag{10}$$

one obtains

$$\sum_{\ell' j} \mathcal{M}_{\ell i,\ell' j}\Psi_{\ell'}(r_j) = G_\ell(r_i|a)\left(\frac{\partial\Psi_\ell}{\partial r} - b\Psi_\ell\right)_a \tag{11}$$

The solution may be written as

$$\Psi_\ell(r_i) = \sum_{\ell' j} \mathcal{M}^{-1}_{\ell i,\ell' j}\, G_{\ell'}(r_j|a)\left(\frac{\partial\Psi_{\ell'}}{\partial r} - b\Psi_{\ell'}\right)_a$$

$$= \sum_{\ell'} \gamma_{\ell i,\ell' a}\left(\frac{\partial\Psi_{\ell'}}{\partial r} - b\Psi_{\ell'}\right)_a \tag{12}$$

Setting $r_i = a$ gives

$$\Psi_\ell(a) = \sum_{\ell'} \gamma_{\ell a,\ell' a}\left(\frac{\partial\Psi_{\ell'}}{\partial r} - b\Psi_{\ell'}\right) = \sum_{\ell'} \mathcal{R}_{\ell\ell'}\left(\frac{\partial\Psi_{\ell'}}{\partial r} - b\Psi_{\ell'}\right)_a \tag{13}$$

The R-matrix is thus seen to be the value of the full Green's function on the surface of the sphere enclosing the internal region. The solution of equation (11) may be accomplished using standard techniques of linear algebra (28). The reduction to a matrix equation has the advantage that vector processors such as the CRAY I can solve such equations 15-20 times faster than scalar computers. If the matrices become too large for central memory, partitioning techniques and/or iterative methods may be used to solve the equations. These approaches may slow down the calculation somewhat but experience has shown that the methodology is still quite efficient. Perhaps the greatest difficulty with the LAM as we have described it is the use of the single-center expansion method to obtain equation (8a). It has been known for many years that such single-center techniques are very slowly convergent for molecular systems. The situation for the calculation of bound states is much worse than for low energy electron scattering due to the strong dependence of the energy on the region near the atomic nuclei. For continuum electrons, which do not penetrate too deeply into the electron cloud, the expansion is slowly convergent but practical techniques can be developed to aid the convergence. The use of the spherical harmonic expansion at the level of equation (8) may in fact be superior to using numerical continuum functions and multicenter functions in the standard R-matrix formalism. The latter approach requires the single center decomposition of the

required two-electron matrix elements. The LAM "matrix elements" are very simple functions requiring little computational effort for their formation. The major effort is placed on the solution of the linear equations, which are well suited to vector prescriptions. In addition schemes can be devised which utilize different quadrature meshes for each partial wave. Since the higher partial wavefunctions are strongly peaked near the nuclear singularity and die off quite rapidly thereafter, it is possible to get accurate representations with very few points. This is very similar in philosophy to the use of multicenter basis sets in conventional approaches. Another approach would be to combine a multicenter basis set expansion with the numerical wavefunction for low partial waves,

$$\Psi(\vec{r}) = \sum_{\ell=0}^{L} \sum_{m=-\ell}^{\ell} F_{\ell m}(r) Y_{\ell m}(\Omega) + \sum_{q} C_q \Phi_q(\vec{r}) \qquad (14)$$

By substituting Equation (14) into Equation (2a) we can derive a set of coupled equations for $F_{\ell m}(r)$ and C_q. These may in turn be reduced to linear algebraic equations by introducing quadratures. The advantage of this latter approach is the possibility of representing the large number of high angular momentum terms by a few $\Phi_q(\vec{r})$. In addition these functions could be chosen to be bound-state Cartesian Gaussians for which much intuition has been developed over the past few decades. However, like the standard R-matrix method it is necessary to perform numerical integrations to calculate the required matrix elements. The efficacy of this can only be ascertained by experimentation. Now that we have outlined the basic theory and numerical technique of the LAM let us turn to the calculation of the exchange and correlation terms which provide the major difficulties of the full many-body problem.

Electron Exchange. The need for an anti-symmetric wavefunction for incident and bound electrons gives rise to nonlocal interactions which greatly complicate the solution of the scattering equations. These exchange interactions have the form,

$$\int K(\vec{r}|\vec{r}')F(\vec{r}')\,d\vec{r}' = \left[\int \Phi_B(\vec{r}') \frac{1}{|\vec{r}-\vec{r}'|} F(\vec{r}')d\vec{r}'\right]\Phi_B(r) \qquad (15)$$

where $\Phi_B(\vec{r})$ is a bound-state molecular orbital and $K(r|r')$ is the exchange kernel. The difficulty with these interactions is not so much their nonlocality as their nonseparability. The nonseparability arises because the interaction $\frac{1}{r_{12}}$ does not decompose into a product of functions of $\vec{r}_1$ and $\vec{r}_2$. If one examines these exchange operators more closely one notices that they are rather short range functions. The reason for this is the quite physical fact that the incident electron can only exchange with a bound state electron when the two are close together. Since the electron cloud of the atom or molecule is spatially localized these interactions fall off quite rapidly away from the target.

These considerations suggest that it should be possible to expand these integral kernels as a sum of separable terms (15,16) using bound state functions as the expansion set,

$$K(\vec{r}|\vec{r}') = \sum_{i,j} \Phi_i(\vec{r}) K_{ij} \Phi_j(\vec{r}') \tag{16}$$

The advantage of equation (16) is twofold. First, the nonseparability is avoided by using a basis set (separable) expansion of the operator. Second, the matrix elements K_{ij} may be extracted from standard bound-state programs available from a wide variety of sources. In addition the matrix elements are independent of energy and need be computed only once even if scattering calculations are to be performed for a range of energies. A practical question which must be answered is the rate of convergence of the separable expansion. Numerous calculations at the static-exchange or Hartree-Fock level on a wide variety of diatomic and triatomic molecules have shown quite rapid convergence. In fact, in many cases, the use of standard SCF basis sets has given results of 10-20% accuracy. By augmenting these sets slightly, we can reach the 1-5% level of accuracy with little difficulty. Another feature of the use of separable expansions may be illustrated by considering the following equation,

$$(\mathscr{L} - \mathscr{E}) \, |F\rangle = |\chi\rangle\langle\phi|F\rangle \tag{17}$$

where $\mathscr{L}$ is a local operator. The solution of equation (17) may be written as

$$|F\rangle = |F^0\rangle + |F^1\rangle\langle\phi|F\rangle \tag{18a}$$

where

$$(\mathscr{L} - \mathscr{E})|F^0\rangle = 0 \tag{18b}$$

$$(\mathscr{L} - \mathscr{E})|F^1\rangle = |\chi\rangle \tag{18c}$$

The unknown constant, $\langle\phi|F\rangle$, may be determined after the solution of equations (18b,c) by quadrature. The generalization to an n-term separable expansion is straightforward requiring n inhomogeneous equations to be solved and the inversion of an (n*n) matrix for the unknown constants. The procedure is quite similar to the treatment of LaGrange undetermined multipliers in standard scattering formalisms. The method is particularly convenient for the LAM since the most difficult computational step in the scattering involves the reduction of the algebraic matrix to $\underset{\sim}{L}\underset{\sim}{U}$ form where $\underset{\sim}{L}(\underset{\sim}{U})$ are lower (upper) triangular matrices. The work required for additional right-hand sides (inhomogeneities) is usually quite small. The reduction in computational time which is achieved by the use of separable exchange varies from factors of about 3 to 10 over standard approaches. This savings in time increases dramatically with the number of incident energies since as mentioned above the

difficult step in the calculation, the formation of the K_{ij} matrix elements, is energy independent. The success of the separable expansion for exchange led us to ask if it would be possible to extend this kind of approach to the treatment of polarization and correlation and ultimately to the treatment of inelastic scattering. The results of that inquiry appear in the next section.

Polarization and Correlation. In order to satisfactorily explain the details of low-energy electron-molecule collisions it is necessary to go beyond the static-exchange level and include correlation effects. It has been known for many years that a straightforward close-coupling expansion is very slowly convergent for elastic scattering for many systems. The basic difficulty is that the physical closed channels are too delocalized in space to adequately describe what is happening near the bound electrons. Pseudostates, (11,12), which are usually derived from a perturbation treatment of the distortion of the molecular charge cloud by an electric field, are far better functions for treating polarization and correlation. These pseudostates may be used directly in the close-coupled equations or included in the open-channel space as a nonlocal energy-dependent optical potential. The latter approach has the advantage of being able to include more functions by using bound-state matrix methods. In addition, the dimensionality of the scattering equations does not increase beyond the static-exchange approximation. However in order to efficiently use the optical potential formalism it is necessary to be able to calculate and manipulate the required Hamiltonian matrix elements rapidly. Since bound state configuration interaction (CI) programs were developed by quantum chemists for just this purpose we began to examine the possibility of using them in the scattering problem. In order to proceed, it is essential for the purpose of the formalism as well as the numerics to introduce a basis set expansion of the continuum. This expansion must be complete enough to represent the important physical effects in the problem. In contrast to the exchange kernel, the optical potential has some long-range character which suggests convergence may be somewhat more difficult than for the static-exchange case. Again, only numerical experimentation would allow us to decide on the efficacy of the approach. From a purely formal standpoint the partitioning of function space into an open (P) and closed (Q) channel part results in the following equation, (12),

$$[\mathcal{H}_{PP} + \mathcal{L}_b - E + \mathcal{H}_{PQ}(E - \mathcal{H}_{QQ})^{-1}\mathcal{H}_{QP}]P|\Psi\rangle = \mathcal{L}_b P|\Psi\rangle$$

for the scattering electron, where

$$P = \sum_\alpha |A(\phi_0(1-N)F_\alpha(N+1))\rangle\langle A(\phi_0(1-N)F_\alpha(N+1))| \qquad (20a)$$

$$P + Q = I \qquad (20b)$$

The Q space configurations, which contain single, double etc. excitations away from the reference set, account for the

polarization and correlation. The use of the discrete expansion enables us to write,

$$V_{opt} = \mathcal{H}_{PQ}(E - \mathcal{H}_{QQ})^{-1}\mathcal{H}_{QP} = \sum_{\alpha,\beta} |F_\alpha\rangle V_{\alpha\beta}(E)\langle F_\beta| \tag{21}$$

which is, of course, a separable form (16,17,18). Thus the formation of the optical potential requires a standard CI program to form the matrix elements and the solution of the linear equations,

$$(E - \mathcal{H}_{QQ})X_{QP} = \mathcal{H}_{QP} \tag{22a}$$

$$\mathcal{H}_{PQ}X_{QP} = V_{opt} \tag{22b}$$

to get the matrix optical potential. The essential difference between the problem with and without correlation is the need to construct V_{opt} at each incident energy. This in turn requires that equation (22) be solved numerous times. However, the Hamiltonian matrix need be computed only one time. Once the optical potential is formed the solution of the scattering equations is identical to that of the static-exchange case. Thus computer codes which were developed for the static-exchange problem may be used without any modifications. This is a great advantage of the optical potential formalism. In all of the applications made so far, $\phi_0(1\text{-}N)$ has been chosen to be the Hartree-Fock wavefunction of the target. Thus the P-space consists of the static-exchange configurations. Since it is impossible to use a complete expansion in Q-space, it becomes quite important to choose the correlating orbitals and configurations to reflect the physics of the low-energy scattering process. A primary consideration is, of course, an accurate represention of the polarization of the target by the incident electron and the subsequent back-reaction of the polarized target on the electron. An elegant way to accomplish this is to use polarized orbitals extracted from a coupled Hartree-Fock calculation. These functions accurately represent the dipole distortion of the molecular target in the presence of an electric field. By adding a further set of diffuse atomic functions to represent the "continuum" electron we can adequately span the space of the electrons. The Q-space is constructed by taking antisymmetrized products of the polarized and scattering orbitals in which an occupied and scattering function are singly excited. These configurations are all single and double excitations away from the static-exchange reference set. However they do not include any double excitations of the core electrons. Such excitations would correlate the core electrons, an effect which we wish to exclude from present calculations. Thus we try to place our efforts on the differential correlations induced by the incident electron rather than the full (N+1) electron problem. In most cases this has been quite satisfactory in bringing the calculations into good agreement with experiment (17,18). However a more general treatment is needed in which target and induced correlations are treated in a balanced fashion. Such a treatment is currently under investigation and will be reported upon in later publications.

Before closing this section it is worth mentioning a new development in the treatment of electronically inelastic collisions which is related to the above discussion. Recently (30) we have shown that it is possible and practical to place the off-diagonal channel-channel interactions in separable form. This leads rather naturally to a formalism in which it is only necessary to solve inhomogeneous, elastic scattering equations for each channel. The reduction in dimensionality from a coupled to a single-channel problem makes the equations much more tractable. The final solution to the coupled channel problem is determined by inverting a matrix whose dimension is the number of expansion functions used for the coupling matrix elements. Optical potentials may be incorporated in the coupling matrix with little additional effort. The method has been successfully applied to the 1s-2s-2p close-coupling equations in atomic hydrogen (30) and molecular applications are underway.

Now let us turn to the extension of the formalism to molecular photoionization.

Photoionization. The photoionization process,

$$AB + h\nu \rightarrow AB^+ + e \tag{23}$$

can be characterized by the dipole matrix element between the initial bound state of AB and the electron-ion continuum wavefunction of the final state. Since the final state is no more than the scattering wavefunction for an electron on a molecular ion, it is quite easy to adapt the LAMOPT formalism to photoionization (29). To accomplish this two things are required: the replacement of the free-particle with the Coulomb Green's function and the calculation of the bound-free dipole matrix element. From the latter quantity, the angular distribution of the photoelectrons

$$\sigma_\Gamma(\Omega) = A_{00} + A_{20}\, P_2(\cos\theta) \quad , \tag{24}$$

and the total photoionization cross section σ_Γ can be calculated. Both quantities are simply related to

$$d_{\ell m} = \langle \Phi_B^{m_i} | r Y_{1m''} | \Psi_{\ell m} \rangle_{m''} = m - m_i \tag{25}$$

where Φ^{m_i} ($\Psi_{\ell m}$) is the bound (continuum) orbital of the electron and $m_i(m)$ is the azimuthal quantum number. In all of the applications of the LAM to photoionization we have calculated wavefunctions for both the bound and continuum electrons at the Hartree-Fock (HF) level. The bound orbitals are taken as solutions of the neutral Hartree-Fock equations. The continuum orbitals are calculated using the frozen-core approximation by which the HF orbitals of the neutral, target molecule are used to represent the ion core (FCHF). This leads to considerable simplification in the form of the dipole matrix elements reducing them to one-electron integrals. Since the bound and continuum electrons are not solutions of the same one-electron Hamiltonian it is necessary to

of the orbitals. This leads to a continuum improved virtual orbital (IVO) equation of the form

$$(h + \sum_i (2a_i J_i - b_i K_i) - E)|\Psi_{\ell m}> = \sum_q \lambda_q |\phi_q> \quad (26a)$$

$$a_i, b_i = \text{coulomb, exchange orbital occupancies} \quad (26b)$$

$$\lambda_q = \text{LaGrange multiplier} \quad (26c)$$

for the continuum electron. This is solved using the LAM.

Now that we have described the formalism in some detail, let us look at our applications to resonant processes.

Applications

Electron + N_2 Scattering. The scattering of low-energy electrons from N_2 is one of the most thoroughly studied problems in molecular physics. The primary reason for this is that the cross section is dominated by a low-energy π_g (2.4 eV), shape resonance which has profound effects on the vibrational excitation spectrum. Under ordinary scattering situations the probability for nuclear excitation by low-energy electrons is quite small due to the large difference in mass of the two particles. However in a resonant process the electron can distort the charge distribution of the target sufficiently to cause great changes in the forces on the nuclei. It is these changes which cause the vibrational excitation not the direct impulsive force of the collision. The temporary capture of the incident electron into the low-lying, π_g anti-bonding orbital of N_2 was put forth as the explanation of the excitation mechanism (2). Since this orbital has a significant amount of valence character it can sufficiently change the potential seen by the nuclei during the collision. These ideas were expanded upon and refined by Herzenberg (32,33) and his collaborators using the complex eigenvalue techniques of Siegert. The calculations however remained semi-empirical and, although they gave good argreement with the experiments of Schultz (2)were dependent on a semi-quantitative adjustable parameter. With the development of the molecular R-matrix method it became possible to perform a first principles calculation of this process. However, in order to accomplish this it was necessary to generalize the R-matrix method to include nuclear motion. The generalization was accomplished by Schneider, LeDourneuf and Burke (34). using the Born-Oppenheimer approximation of the R-matrix levels of the (N+1) electron problem as the zeroth order approximation. The theory was successfully applied by Schneider, LeDourneuf and Lan (35) to the $e+N_2$ problem. The results of that calculation, which are shown in Fig. 1, demonstrated for the first time that an ab initio method could, within the context of the Born-Oppenheimer approximation, explain the resonant vibrational excitation process. Other calculations (6) followed which confirmed the results of the R-matrix study. Recently (31) we have performed a series of calculations using the

cally demonstrated that the π_g resonance is dominated by short-range distortion. These ideas were implicit in the R-matrix calculations (35) which were based on the negative ion SCF wavefunction of N_2. The N_2^- SCF wavefunction does not contain any excitation which destroys the Σ_g symmetry of the N_2 core. In fact to first order in perturbation theory the N_2^- SCF wavefunction can be obtained as a single-excitation CI using N_2 SCF orbitals. Hazi and coworkers (6) used this equivalence and the Feshbach formalism to obtain results in good agreement with the R-matrix calculations of Schneider, Lebourneuf and Lan. The recent LAM calculations given in Table I also show that one must be cautious in not overcorrelalating the negative ion wavefunction with respect to the neutral molecule. More extended double excitation CI calculations lowered the resonance position and width below the experimental value demonstrating these difficulties rather dramatically. Finally, the calculations show possible problems with semi-empirical theories using long-range

Table I. Position and Width of $^2\Pi$ Resonance in N_2 as a function of the type of calculation

Type of Calc.	E_R(eV)	Γ_R(eV)
Short and long range 3 references	2.03	.281
Short and long range 6 references	1.97	.264
Short and long range 19 references	1.66	.178
Short range 3 references	2.13	.314
Short range 19 references	2.07	.301

cutoff polarization potentials to explain the resonance (31). These potentials, which have adjustable parameters, may be tuned to reproduce the resonant features but it is dangerous to place too much emphasis on the forms of the interaction. The long-range polarization potential has only a minor effect on the resonance in N_2; it is mainly a short-range effect. The adjustment of the cutoff in the model potential mimics these short-range features in a crude but unfortunately unpredictable fashion. It may be unwise to rely on the predictions of these model potentials for other symmetries which may be dominated by quite different physical effects.

Electron + H_2 Scattering. The low-energy elastic scattering of electrons from H_2 shows a broad feature which is due to a p-wave shape resonance. In our calculations (17), no attempt was made to treat this in any special fashion. The calculation was the first one in which we included polarization and correlation using an optical potential and the intent was to explain the low-energy behavior of the cross section. The results, which are shown in

Fig. 2, are in excellent agreement with experiment (39,40) over a considerable energy range and clearly reproduce the broad shape resonance mentioned above. The optical potential was constructed from a set of one-electron functions incorporating the SCF distortions of the target in the presence of an electric field. These were coupled to the incident electron in the manner described earlier and results in an optical potential of about 400 spin eigenfunctions. The calculation required about 8 seconds of CRAY I time per energy.

Electron + H_2^+ Scattering. The first application of the LAMOPT to molecular ions was undertaken to try to resolve some differences in the results obtained for e+H_2^+ scattering by the Stieltjes calculations of Hazi (41) and those of the Japanese (42) using the Kohn variational method (18). The calculations were performed with a number of basis sets in order to understand any problems which might have affected either previous set of calculations. Our early results confirmed the position and width of the first resonance as given by the Stieltjes method but produced higher resonances in poor agreement with the Japanese and earlier close coupling calculations. Since the basis set used for these calculations was not designed to treat Rydberg like resonances, we modified it to include more diffuse orbitals of the proper symmetry and re-ran the calculations. The results, which are shown in Fig. 3 confirm the position and width of the lowest resonance and are in good agreement with the close-coupling calculations of Collins and Schneider (36) and the Kohn variational results for the second resonance. In addition a third resonance was found which is considerably lower than that of the Kohn calculation. Although we have not explored this Rydberg series of resonances any further, it is clear that the Kohn calculation for the third member of the series is much too high. In fact it lies above the ionization potential of the H_2^+ ion and must be an artifact of the poor basis used in the Kohn calculation. The quality of the results obtained by the optical potential approach for the e+H_2^+ scattering gives us much confidence in its application to more complicated problems. In addition the calculations demonstrate that we can deal with ionic as well as neutral systems and Feshbach as well as shape resonances with the formalism.

Photoionization of N_2. In this section we consider the following processes,

$$h\nu + N_2 \rightarrow N_2^+ (3\sigma_g^{-1}) + e \begin{Bmatrix} k\sigma_u \\ k\pi_u \end{Bmatrix} \qquad (27)$$

$$\rightarrow N_2^+ (\pi_{xu}^{-1}) + e \begin{Bmatrix} k\sigma_g \\ k\pi_{xg} \\ k\delta_{xyg} \end{Bmatrix}$$

for the ground state of N_2 (29). The first process has a broad σ_u shape resonance, while the latter process leads to a spurious

shape resonance at the frozen-core Hartree-Fock level (FCHF). Both calculations were performed with a number of basis sets to represent the exchange operator. In all cases very little sensitivity to the basis was observed in the scattering function. However sensitivities of the order of 10-20% have been observed in the cross section due to the inclusion or exclusion of diffuse orbitals in the construction of the occupied molecular orbitals. Evidently the more diffuse character of the integrand in the dipole matrix element is quite sensitive to small components in the bound orbitals. Similar conclusions have been observed by ONeil and Reinhardt in the photoionization of H_2 (37). The results of our calculations are shown in Figs. 4-6, where we compare with those of other approaches and experiment (43). The agreement between the LAM and Schwinger variational (SV) method is quite good. Reasonable agreement with the Stieltjes method is observed for ionization from the $3\sigma_g$ orbital. The ionization of the π_{xu} orbital of N_2 is one of the classic failures of the FCHF model. The HF potential improperly places a valence-like π_g orbital above the ionization continuum. Better calculations, such as those based on an random phase approximation (RPAE) model (5) or optical potential formulation can correct the difficulty and remove the spurious resonance. This has already been done with the RPAE and calculations using our optical potential approach will be undertaken in the near future when we can deal with sets of coupled, open channels.

Photoionization of NO. We consider photoionization of the 2π orbital of NO into $k\sigma$, $k\pi_x$ and $k\delta_{xy}$ continua (29). Our interest in this process stemmed from a desire to resolve the rather large differences between the Stieltjes (44) and SVM calculations (45). The results of our calculations and a comparison of theory and experiment (46,47) is shown in Figs. 7-8. We observe no structure in the individual partial photionization cross sections and must conclude that these features are an artifact of the imaging procedure or linear dependence in the basis set. Our calculations are in reasonable agreement with the SV method, showing a number of broad shape resonances whose position can vary slightly with the basis set. This is especially evident in the sharper σ resonance. As with N_2, the difference between the LAM and SVM results is primarily due to the inclusion of diffuse orbitals in the bound molecular orbitals. Very little sensitivity to basis was observed in the scattering solutions.

Photoionization of CO_2. We have considered the following processes for photoionization of ground state CO_2 (29):

$$h\nu + CO_2 \rightarrow CO_2^+ \begin{Bmatrix} 1\sigma_g^{-1} \\ 2\sigma_g^{-1} \\ 4\sigma_g^{-1} \end{Bmatrix} + e \begin{Bmatrix} k\sigma_u \\ k\pi_{xu} \end{Bmatrix}$$

We are particularly interested in these processes since there are considerble differences between the results of the Stieltjes method on one hand and those of the SV and LA method. The LAM and SVM both

predict rather narrow shape resonances in the $1\sigma_g$ and $4\sigma_g$ ionizations while the Stieltjes approach gives rather broad, nonresonant shapes. The calculation of the continuum wavefunctions for these channels represents a most stringent test of the single-center expansion approach. However we have systematically increased the number of partial waves in the calculation until we are confident of a 5% or better convergence in the cross section. In addition we have explored many basis sets, more or less contracted or more or less diffuse. Small differences beween the SV and LA calculations can be noticed but nothing like the qualitative differences with the Stieltjes approach. The final results for the total cross section in these channels is given in Figs. 9-11. It is difficult to say why the agreement between the methods is so poor for $1\sigma_g$ and $4\sigma_g$ ejection processes. Earlier Stieltjes calculations on the $1\sigma_g$ photoionization by Daasch, Davidson, and Hazi (38) have shown a great sensitivity to both basis set and imaging technique. Perhaps the difficulty is due to the inability of the Stieltjes method to place enough eigenvalues in the resonant region. Since the resonances in the $1\sigma_g$ and $4\sigma_g$ ionization processes but not the $2\sigma_g$ process are at quite high electron energies, it could be difficult to produce a proper pseudospectrum with conventional Gaussian type orbitals. This would also explain why the low energy $2\sigma_g$ results agree in all three approaches. The resolution of these differences is not simple but we feel it is imperative to try to do so. At present the Stieltjes method is the only approach capable of dealing with complicated polyatomic species. Its reliability must be tested against other approaches where such tests are possible.

Conclusion

Resonance phenomena have been shown to play a significant role in many electron collision and photoionization problems. The long lived character of these quasi-stationary states enables them to influence other dynamic processes such as vibrational excitation, dissociative attachment and dissociative recombination. We have shown it is possible to develop ab initio techniques to calculate the resonant wavefunctions, cross sections and dipole matrix elements required to characterize these processes. Our approach, which is firmly rooted in the R-matrix concept, reduces the scattering problem to a matrix problem. By suitable inversion or diagonalization we extract the required resonance parameters. Finally we have illustrated the power of the method by calculating the cross sections for electron scattering or photoionization from a number of diatomic and polyatomic molecules. These calculations have been among the first to include polarization and correlation in an ab initio way. The extension of our methods to inelastic electronic processes and nuclear excitation and dissociation are underway and should appear soon.

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Figure 1. A comparison of experimental and theoretical vibrational excitation cross sections for N_2 scattering.

Figure 2. Comparison of theoretical and experimental total cross sections for e-H_2 scattering. Curves are as follows: (1) represents the effective optical potential; (2) represents the experiment by Golden *et al.*, and (3) represents the experiment by Dalba *et al.*

Figure 3. Eigenphase sums as a function of energy for the $^1\Sigma_g$ symmetry for e-H_2^+ collisions.

Figure 4. Total cross sections for the photoionization of N_2 leading to the $X^2\Sigma_g^+$ state of $N_2^+(3\sigma_g^{-1})$. Comparison of theoretical methods: solid line, LA; dashed line, SV; chain-dashed line, STMT.

Figure 5. Partial and total cross sections for the photoionization of $N_2(N_2^+X^2\Sigma_g^+)$. Comparison of the LA method and experiment: solid line, total; chain-dashed line, $3\sigma_g \rightarrow k\sigma_u$; dashed line $3\sigma_g \rightarrow k\pi_u$; crosses. expt.

Figure 6. Partial cross sections for the photoionization of N_2 leading to the $A^2\Pi_u$ state of $N_2^+(1\pi_u^{-1})$. Comparison of theoretical methods for $1\pi_u \rightarrow k\pi_g$: solid line, LA; dashed line, SV.

Figure 7. Total cross section for the photoionization of NO leading to the $X^1\Sigma^+$ state of $NO^+(2\pi^{-1})$. Comparison of theoretical methods: solid line, LA; dashed line, SV; chain-dashed line, STMT.

Figure 8. Partial and total cross sections for the photoionization of NO ($NO^+X^1\Sigma^+$). Comparison of the LA method and experiment: solid line, total; chain-dashed line, $2\pi \rightarrow k\pi$; dashed line $2\pi \rightarrow k\sigma$; dotted line, $2\pi \rightarrow k\delta$; crosses, expt.; triangles, expt.

Figure 9. Partial and total cross sections for the photoionization of CO_2, ($CO_2^+C^2\Sigma_g^+$). Comparison of the LA method with experiment; solid line, total; chain-dashed line, $4\sigma_g \rightarrow k\sigma_u$; dashed line, $4\sigma_g \rightarrow k\pi_u$; crosses, expt.

Figure 10. Partial and total cross sections for the photoionization of the $2\sigma_g$ orbital of CO_2 in the LA method.

Figure 11. Partial and total cross sections for the photoionization of the $1\sigma_g$ orbital of CO_2 in the LA method.